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K. S. Siddiqi & N. Nishat

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SYNTHESIS AND CHARACTERIZATION OF NEW SCHIFF BASE MACROCYCLES AND THEIR METAL CHELATES

K. S. Siddiqi * and N. Nishat

Department of Chemistry, Aligarh Muslim University, Aligarh. 202002, India

ABSTRACT

New Schiff base macrocycles, 1,4,7,10-tetraaza-2,3-dioxo-5,6,11,12-bis(1'-phenyl-2',3'dimethylpyrazole)dodeca-7,10-diene(L¹), 1,4,7,11-tetraaza-2,3-dioxo-5,6,12,13-bis(1'-phenyl-2',3'dimethylpyrazole) trideca-7,11-diene (L²) and their Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) complexes have been synthesized and characterized by elemental analysis, magnetic susceptibility, electronic and infrared spectroscopy. The ligands have been characterized by IR and ¹H NMR measurements. The complexes were characterized by IR, UV-Vis spectra and magnetic moments. Molar conductance shows non-electrolytic behaviour of the divalent metal complexes while the trivalent metal complexes appear to be 1:1 electrolytes. An octahedral geometry has been proposed for all the complexes.

INTRODUCTION

The synthesis and application of macrocycles involving various hetero atoms in the ring is a subject of current research interest¹⁻⁶. A number of efficient methods are now available for the synthesis of such macrocycles⁷⁻¹⁰. Sometime the reaction is carried out by metal template assistance. Complexes of metal ions with synthetic macrocycles are of great interest due to their resemblance with many naturally occurring systems like porphyrins and cobalamines¹¹⁻¹⁶ and also because they are capable of furnishing an environment of controlled geometry. The macrocyclic polydentate ligands containing oxalato groups are not abundant and, hence, it was of interest to study the formation of such macrocycles and their transition metal complexes. We herein report the synthesis and characterization of two new macrocycles and their complexes with first row transition metal ions.

RESULTS AND DISCUSSION

The Schiff base macrocycles and their transition metal complexes were synthesized according to Scheme I. They are stable to air and heat. Their colours, melting points, molar conductances and analyses are listed in Tables I and II. Molar conductances of one millimolar solution of the divalent metal complexes measured in DMSO at room temperature (11-43 ohm⁻¹ cm² mol⁻¹) indicated them to be non-electrolytes¹⁷ which may be formulated as [M(L)Cl₂] where M = Mn(II), Co(II), Ni(II), Cu(II) and Zn(II). For the complexes of trivalent metal ions, the molar conductances fall in the range 72-81 ohm⁻¹ cm² mol⁻¹ suggesting that they are 1:1 electrolytes and can be represented as [M(L)Cl₂]Cl where M = Fe(III) and Cr(III).

¹H NMR Spectra

In the ¹H NMR spectrum of the free ligand L^2 all CH₃ protons (as these are equivalent) appear as a singlet at δ 1.48 (12H), while the two types of methylene protons give a singlet at δ 2.5 (4H) and triplet at δ 2.6 (2H). The phenyl protons appear as multiplet in the range δ 7.2 - 7.5. The NH protons show a singlet at δ 7.6. The spectrum of L¹ is similar to that of L², the difference is only in the methylene protons. Here, the singlet of only one type of methylene protons appears at δ 2.4 (4H). The shift of the CH₂ and NH proton signals towards lower field in the spectra of metal complexes is an indication of the coordination of the macrocycles.

IR Spectra

The IR spectra of free Schiff base macrocycles (Table III and IV) display a band centered at 3330 cm⁻¹ due to v(N-H) of the amide group¹⁸ while the C=O stretching frequency of the amide group appeared at 1600 cm⁻¹. However, the v(C=O) frequency corresponding to the amide I band (1600 cm⁻¹) and v(N-N) (1070 cm⁻¹) remain unaltered in both the free and chelated macrocycles which is in accord with the results reported by Hanson et al¹⁹. These free macrocycles are known to exhibit v(C=N) at 1660 cm⁻¹ which undergoes a shift to lower wave number after chelation with the metal ion. In the present work, v(C=N) and v(C-N) have been observed in the 1650 -1600 cm⁻¹ and 1380 -1410 cm⁻¹ ranges, respectively, which has been found to be shifted to lower wave numbers in the complexes due to the reduction in electron density indicating the coordination of the metal ion via the nitrogen atoms.

The v(M-N) frequency in the Fe(III) and Cr(III) complexes appears in the 375 - 390 cm⁻¹ region as compared with those of divalent metal ions at 315 - 345 cm⁻¹. This may be ascribed to more effective bonding due to substantial overlap of Cr(III) and Fe(III) orbitals with those of the



Scheme 1: Synthesis of Ligands and Complexes

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Table I. Colour, Melting Points, Molar Conductance and Analytical Data for L¹ and its Metal Chelates.

Compounds	Yield	(%)	Colour	M.p. (°C)	Molar		Analysis	Foi	and (Calc	d.)
ſ					Conductance ohm ⁻¹ cm ² mol ⁻¹					
	9	4				%C	H•%	N%	%CI	%M
L' C.H. N.O.	26		Yellow	160		64.90 (64.45)	6.28 (6.06)	22.21 (22.47)		
484.55							Ì	Ì		
[CrL ¹ Cr]Cl C ₁₆ H ₂₈ Cl ₃ CrN ₈ O ₂ 642.90	32	49	Green	280 (d)	72	49.61 (49.73)	4.86 (4.60)	17.23 (17.06)	16.23 (16.19)	7.26 (7.91)
[MnL ¹ Cl ₃]Cl C ₂₆ H ₂₆ Cl ₂ MnN ₈ O ₂ 610.39	38	48	Grey	210 (d)	12	52.32 (51.94)	4.56 (4.84)	17.55 (17.95)	11.56 (11.36)	8.41 (8.80)
[FeL ¹ Cl ₃ Cl C ₂₆ H ₂₆ Cl ₃ FeN ₈ O ₂ 646.75	40	48	Brown	320 (d)	79	49.23 (49.08)	4.66 (4.58)	16.5 8 (16.96)	16.63 (16.10)	8.81 (8.45)
[CoL ¹ ငါ႕] င ₁₄ H ₃₆ င1 ₄ CoN ₈ O ₂ 614.39	44	52	Pink	340 (d)	16	51.22 (51.61)	4.96 (4.81)	17.51 (17.83)	11.35 (11.28)	9.42 (9.38)
[NïL ¹ Cl ₁] C ₁₄ H ₂₄ Cl ₁ NïN ₈ O ₂ 614.14	46	51	Green	290 (d)	11	51.51 (51.63)	4.72 (4.81)	17.23 (17.84)	11.45 (11.29)	9.52 (9.34)
. [CuL ¹ Cl ₃] C ₁₄ H ₃₄ Cl ₂ CuN ₈ O ₂ 619.00	39	53	Green	265 (d)	41	51.55 (51.23)	4.83 (4.78)	17.22 (17.70)	11.52 (11.20)	9.64 (10.04)
[ZnL ¹ Cl ₁] C ₂₆ H ₂₆ Cl ₁ N ₆ O ₂ Zn 620.83	36	49	White	270 (d)	42	5 1.22 (5 1.07)	4.86 (4.76)	17.23 (17.65)	11.23 (11.17)	10.52 (10.30)
a. Synthesized by the dir	ect met	hod	b. Synthesize	d by template	method					

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Table II. Colour, Melting Points, Molar Conductance and Analytical Data for L² and its Metal Chelates.

Compounds	Ā	eld (%)	Colour	M.p. (C)	Molar		Analysi	E E	ound (Ca	lcd.)	Γ
					Condications		•		,		
					ohm ⁻¹ cm ² mol ⁻¹						
	-	م				%C	H‰	N%	%CI	‰M	
L ²	24	1	Light	180	:	65.23	6.28	22.21	I	1	<u> </u>
C ₂₇ H ₃₀ N ₈ O ₂ 498.57			Yellow			(65.04)	(6.06)	(22.47)			
[CrT sc1 sc1	41	48	Green	250 (d)	80	49.61	4.86	17.23	16.23	7.26	
C ₇ ,H ₃₀ Ci ₃ CrN ₄ O ₂ 656.93				, ,		(48.73)	(4.60)	(17.06)	(16.19)	(16.7)	
[MnL2CL]	43	50	Grey	290 (d)	42	52.32	4.56	17.55	11.56	8.41	
C ₇ ,H ₃₀ Cl ₂ MnN ₈ O ₂ 624.42						(51.94)	(4.84)	(17.95)	(11.36)	(8.80)	
[FeLtCI,]CI	38	52	Brown	240 (d)	89	49.23	4.66	16.58	16.63	8.81	
C ₂₇ H ₃₀ Cl ₃ FeN ₈ O ₂ 660.78						(49.08)	(4.58)	(16.96)	(16.10)	(8.45)	
[Colt2cl]	36	51	Pink	260 (d)	23	51.22	4.96	17.51	11.35	9.42	
C ₂₇ H ₃₆ Cl ₂ CoN ₅ O ₂ 628.41						(51.61)	(4.81)	(17.83)	(11.28)	(9.38)	
[Init. 40]	45	52	Green	320 (d)	42	51.51	4.72	17.23	11.45	9.52	<u> </u>
C ₂₇ H ₃₀ Cl ₇ NiN ₈ O ₂ 628.17						(51.63)	(4.81)	(17.84)	(11.29)	(9.34)	
[Cull 2Cl,]	4	51	Green	310 (d)	40	51.55	4.83	17.22	11.52	9.64	
C ₂ ,H ₄₀ Cl ₂ CuN ₈ O ₂ 633.02						(51.23)	(4.78)	(17.70)	(11.20)	(10.04)	
[ZnL ² Cl ₂]	43	49	White	340 (d)	43	51.22	4.86	17.23	11.23	10.52	_
C ₂ ,H ₃₀ Cl ₂ N ₈ O ₂ Zn						(51.22)	(4.76)	(17.65)	(11.17)	(10.30)	
a. Synthesized by the dir	ect m	ithod b.	Synthesized	by template	method						1

NEW SCHIFF BASE MACROCYCLE METAL CHELATES

Compounds	v(NH)	ν(C=N)	v(C-N)	v(M-N)	ν(M-Cl)
Lı	3330m	1660s	1410m	-	-
[CrL ¹ CL]Cl	3310m	1630s	1400m	370s	250w
[MnL ¹ Cl ₂]	3315m	1610s	1390m	3158	260w
[FeL ¹ Cl ₂]Cl	3300m	1630s	1380m	390s	265w
[CoL ¹ Cl ₂]	3320m	1590s	1390m	320s	280w
[NiL ¹ Cl ₂]	3310m	1580s	1410m	340s	290w
$[CuL^1 Cl_2]$	3310m	1640s	1390m	330s	285w
[ZnL ¹ Cl ₂]	3300m	1590s	1390m	330s	295w

Table III. (Important IR Bands (cm⁻¹) for L¹ and its Metal Chelates

Table IV. Important IR Bands (cm^{-1}) for L^2 and its Metal Chelates

Compounds	v(NH)	v(C=N)	ν(C-N)	v(M-N)	v(M-Cl)
L ²	3330m	1650s	1380m	-	-
[CrL²CL]Cl	3320m	1630s	1360m	380s	300w
[MnL ² CL]	3300m	1620s	1370m	345s	300w
[FeL ² Cl ₂]Cl	3315m	1610s	1360m	375s	280w
$[CoL^2Cl_2]$	3310m	1640s	1370m	345s	290w
[NiL ² Cl ₂]	3300m	16358	1365m	345s	300w
[CuL ² Cl ₂]	3320m	1620s	1360m	340s	295w
$[ZnL^2Cl_2]$	3310m	1630s	1360m	315s	275w

ligands which increases the electron density around them with a consequent increase in v(M-N). The weaker intensity bands observed in the region 250 - 300 cm⁻¹ may be associated with the M - Cl bond²⁰.

Electronic Spectra and Magnetic Moments

In all the complexes of Cr(III) three bands were observed (Table V). From the simple orbital splitting pattern, it is clear that Cr(III) has three unpaired electrons which is supported by the observed magnetic moment. These results correspond to an octahedral geometry around the metal ion.

The majority of high spin Mn(II) complexes have an effective magnetic moment of 5.90 BM. In the present case the observed value (6.00 - 6.04 BM) is very close to the calculated one²¹. The magnetic moment value and electronic spectra suggest an octahedral geometry for the Mn(II) ion.

Three bands are anticipated for all the complexes of Fe(III). The magnetic moment of 5.86 - 5.88 BM and the colour of the complexes are consistent with an octahedral geometry around the metal ion²².

The Ni(II) complexes exhibit three main bands (Table V) which may be attributed to the transitions ${}^{3}T_{1g}(P) \leftarrow {}^{3}A_{2g}(F)$, ${}^{3}T_{1g}(F) \leftarrow {}^{3}A_{2g}(F)$ and ${}^{3}T_{2g}(F) \leftarrow {}^{3}A_{2g}(F)$. On the basis of magnetic and spectral assignments, an octahedral structure for the Ni(II) ion has been proposed.

The electronic spectra of the Co(II) complexes show three absorption bands and the magnetic moment ranges between 2.62 - 2.81 BM. This variation is possibly due to a minor difference in the size and field strength of the macrocycles²³.

In the electronic spectra of the Cu(II) complexes one charge transfer and one broad band have been observed which is the characteristic of Cu(II) ion. The magnetic moment is slightly above the theoretical value although it is not very unusual for an octahedral Cu(II) complex.

EXPERIMENTAL

Aminoantipyrine, ethylenediamine, 1,3-diaminopropane (Koch Light) diethyl oxalate and metal chlorides (BDH) were used as received. Elemental analyses were made with a Thomas and Coleman analyser Carlo Erba 1106. The ¹ H NMR spectra were recorded on a Bruker WP SY Downloaded by [Universität Osnabrueck] at 02:54 10 March 2016

Compounds	Magnetic moment (B.M.)	Electronic bands (cm ⁻¹)	Possible assignments	10 Dq (cm ⁻¹)	B (cm ⁻¹)	æ	l og c
[ເະະະາ ເຕາ]ເປ	3.75	37037 24096 17241	$\begin{array}{l} {}^{4}\mathrm{T}_{1\mathbf{a}}(\mathrm{P}) \leftarrow {}^{4}\mathrm{A}_{2\mathbf{a}}(\mathrm{F}) \\ {}^{4}\mathrm{T}_{1\mathbf{a}}(\mathrm{F}) \leftarrow {}^{4}\mathrm{A}_{2\mathbf{a}}(\mathrm{F}) \\ {}^{4}\mathrm{T}_{2\mathbf{a}}(\mathrm{F}) \leftarrow {}^{4}\mathrm{A}_{2\mathbf{a}}(\mathrm{F}) \end{array}$	15200	9880	0.95	1.52
[MnL ¹ Cl ₂]	6.00	25000 23220 16000		11200	780	0.81	1.68
[FeL ¹ Cl ₂]Cl	5.88	34482 26315 18018	$\begin{array}{l} {}^{4}T_{1_{\mathbf{R}}}(P) \leftarrow {}^{6}A_{1_{\mathbf{R}}} \\ {}^{4}T_{2_{\mathbf{R}}}(G) \leftarrow {}^{6}A_{1_{\mathbf{R}}} \\ {}^{4}T_{1_{\mathbf{R}}}(G) \leftarrow {}^{6}A_{1_{\mathbf{R}}} \end{array}$	14320	920	0.84	1.71
[CoL ¹ Cl ₂]	2.62	21276 19047 14084	$ {}^{4}T_{1\mathbf{g}}(P) \leftarrow {}^{4}T_{1\mathbf{g}}(F) $ $ {}^{4}A_{2\mathbf{g}}(F) \leftarrow {}^{4}T_{1\mathbf{g}}(F) $ $ {}^{4}T_{2\mathbf{g}}(F) \leftarrow {}^{4}T_{1\mathbf{g}}(F) $	13290	880	0.91	1.66
['nit 'cı,]	3.21	28169 25641 15800	$\begin{array}{l} ^{3}T_{1\mathbf{g}}(\mathbf{P}) \leftarrow \ ^{3}\mathbf{A}_{2\mathbf{g}}(\mathbf{F}) \\ ^{3}T_{1\mathbf{g}}(\mathbf{F}) \leftarrow \ ^{3}\mathbf{A}_{2\mathbf{g}}(\mathbf{F}) \\ ^{3}T_{2\mathbf{g}}(\mathbf{F}) \leftarrow \ ^{3}\mathbf{A}_{2\mathbf{g}}(\mathbf{F}) \end{array}$	12210	840	0.77	1.62
[נייד _ו כוי]	1.99	32000 12500	Charge transfer ${}^2T_{2a} \leftarrow {}^2E_{6}$	ı	ı	ı	ı
[ZnL ¹ Cl ₁]	Diamagnetic						

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[CrL² Cl_]Cl	3.82	37037 26315 16000	$\begin{array}{l} {}^{4}T_{1\mathbf{k}}(P) \leftarrow {}^{4}A_{2\mathbf{k}}(F) \\ {}^{4}T_{1\mathbf{k}}(F) \leftarrow {}^{4}A_{2\mathbf{k}}(F) \\ {}^{4}T_{2\mathbf{k}}(F) \leftarrow {}^{4}A_{2\mathbf{k}}(F) \end{array}$	14100	920	0.94	1.80
[MnL ² Cl ₂]	6.04	32258 22988 19047	⁴ T ₁₄ (P)← ⁶ A ₁₄ ⁴ T ₂₄ (G)← ⁶ A ₁₄ ⁴ T ₁₄ (G)← ⁶ A ₁₄	10980	720	0.75	1.85
[Fe.L'CI]CI	5.86	31746 25000 20000	⁴ T ₁₄ (P)← ⁶ A ₁₄ ⁴ T ₂₄ (G)← ⁶ A ₁₄ ⁴ T ₁₄ (G)← ⁶ A ₁₄	13888	016	0.83	1.89
[CoL ² Cl ₂]	2.81	22727 21052 11111		12270	860	0.89	1.52
[Nill ² Cl ₂]	3.12	25974 15151 12048	$\begin{array}{l}{}^{3}T_{1\mathbf{k}}(P) \leftarrow {}^{3}A_{2\mathbf{k}}(F)\\ {}^{3}T_{1\mathbf{k}}(F) \leftarrow {}^{3}A_{2\mathbf{k}}(F)\\ {}^{3}T_{2\mathbf{k}}(F) \leftarrow {}^{3}A_{2\mathbf{k}}(F)\end{array}$	06611	800	0.74	1.84
[CuL ² Cl ₂]	1.98	32258 12987	Charge transfer ²T _{2≰} ← ²E _≰				1

spectrometer. The IR spectra (4000 - 200 cm⁻¹) were recorded on a Perkin Elmer grating spectrometer, model 621. The electronic spectra were recorded on a Carl-Zeiss VSU-2P spectrophotometer. Magnetic susceptibility measurements were carried out with a vibrating sample Allied Research model 155 magnetometer at room temperature. The molar conductances were measured at room temperature using a Systemics 321 conductivity bridge. Metals were determined by complexometric turation using EDTA. Chlorine was determined gravimetrically.

Synthesis of L¹ and L²

Synthesis of L1

Ethylenediamine (10 mmol, 0.66 mL) was added dropwise to 4-aminoantipyrine (20 mmol, 4.6 g) dissolved in 100 mL hot ethanol and the mixture was refluxed for about 20 h. It was cooled to 0°C and acidified with HCl, taking care that the temperature did not exceed 0°C, which yielded a light brown precipitate. It was redissolved in 50 mL ethanol, diethyl oxalate (10 mmol, 1.35 mL) was added and the mixture was cooled to 0°C, which afforded a yellow product (Scheme I). It was washed with ethanol and dried in vacuo. Yield, 1.59 g (26%).

Synthesis of L²

 L^2 was synthesized by the above method using 1,3-diaminopropane (10 mmol, 0.85 mL) and 4-aminoantipyrine (20 mmol, 4.06 g) and diethyl oxalate (10 mmol, 1.35 mL). Yield 1.48 g (24%).

Synthesis of Complexes by the Direct Method

The metal chloride (2 mmol) in ethanol (25 mL) was added dropwise to the ligand (2 mmol) dissolved in a 1:1 mixture (50 mL) of ethanol and a buffer of pH = 4. The mixture was refluxed for 3 h. A coloured precipitate appeared under reflux which was filtered, washed with ethanol and dried in vacuo. As the yield of the complexes synthesized by metathetical reactions was very small, the template method was also employed.

Template Synthesis of Complexes

Ethylenediamine (2 mmole, 0.12 mL) was added dropwise to an ethanolic solution (50 mL) of 4-aminoantipyrine (4 mmol, 0.18 g). After refluxing this mixture for about half an hour, diethyl oxalate (2 mmol, 0.2 mL) was added and further refluxed for 24 h. The mixture was cooled to 0°C

and metal chloride (2 mmol) in ethanol (25 mL) was added which afforded brisk precipitation of the complexes (Yield 48 - 53 %).

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